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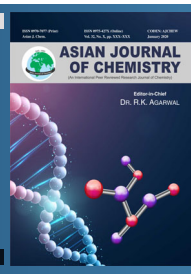

An Electrochemical Sensor based on Electrodeposited CTAB Film on Glassy Carbon Electrode for Detection of Morphine

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A simple, effective and rapid method for the electrochemical detection of morphine is described based on glassy carbon modified electrode with poly(CTAB). In this work, poly(CTAB) thin film was generated through elecropolymerization of the surfactant CTAB. The formation of nanoporous thin film of poly(CTAB) was confirmed by field emission scanning electron microscopy (FESEM) with energy dispersive spectra (EDS) and Fourier transform infrared spectroscopy (FTIR). The electrochemical behavior of morphine is explained in terms of the anodic oxidation of its tertiary amino group. The limit of detection was calculated as 0.2 µM with a good regression between concentration and peak current of morphine by using differential pulse voltammetry within the range of 50 nM to 20 µM. The poly(CTAB)/GCE based sensor shows excellent electrochemical performance for the detection of morphine and this sensing platform can be effective for the detection of similar molecules.

Keywords: Electrochemical sensor, Poly(CTAB), Morphine.

INTRODUCTION

Morphine is an opiate analgesic and one of commonly used narcotic pain killers. Among such drugs, morphine is the most abused and possess a high addiction rate. If morphine is used consistently, the user becomes both physically and psychologically dependent [1]. Therefore, the level of morphine is to be strictly monitored, fast and sensitive detection methods are to be adopted for the proper usage of morphine.

There are various techniques like UV-visible spectroscopy [2], high performance liquid chromatography [3], fluorometry [4], surface plasma resonance [5] and electrochemical methods [6-10] are available for the determination of morphine. Among them electrochemical method are unique due to its fast response, simplicity, selectivity, low cost and miniaturization. Many researchers used diversely modified electrodes for the determination of morphine with high sensitivity and selectivity. The commonly used modifiers are glassy carbon electrode [7], gold nanoparticle modified carbon paste electrode [8], ordered mesoporous carbon modified glassy carbon electrode [9], gold nanoparticle decorated graphene electrode [10], aluminium electrode modified with metallic palladium and prussian blue [11], glassy carbon electrode modified with multiwalled carbon nanotube/chitosan composite [12], graphene nanosheet modified glassy carbon electrode [13], ionic-liquid type multiwalled carbon nanotube paste electode [14] and polymer modified electrode [15], *etc*. The physical and chemical properties of polymer may be tailored over a wide range of characteristics, they play a versatile role in sophisticated electronic measuring devices such as sensors [16,17].

Many electroactive polymers have emerged as attractive candidate as sensor due to their electrochemical, electrical and optical properties. There are several reports on the use of cationic surfactant based polymer for electrochemical detection of various analytes with sensitivity and selectivity [18-20]. The surfactant CTAB received attention by virtue of its unique structure consists of a water compatible hydrophilic head and an oil compatible hydrophobic tail. The present work focus on the electropolymerization of CTAB in acidic medium and application of this polymer modified glassy carbon electrode for the detection of morphine. The sensor poly(CTAB) showed high sensitivity and better catalytic activity towards morphine.

EXPERIMENTAL

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using CHI 604 D electrochemical analyzer in a conventional three electrode glass cell. A platinum wire, Ag/AgCl and a 3 mm diameter glassy carbon electrode (GCE) modified with poly(CTAB) were used as counter electrode, reference electrode and working electrode. Scanning electrone microscope (SEM) images with energy dispersive X-ray (EDX) were obtained with Carl Zeiss EVO 18 secondary electron microscope.

Cetyltrimethyl ammonium bromide (CTAB), potassium permanganate, ascorbic acid, uric acid were obtained from Merck, India. Morphine was obtained from Sigma-Aldrich. Analytical grade reagents were used as such without further purification. Stock solutions of 0.1 M Na_2HPO_4 and NaH_2PO_4 were prepared, phosphate buffer solution (PBS) was prepared by mixing these two solutions. The pH of solution was adjusted with dilute H_3PO_4 and NaOH. Moreover, deionized water was used throughout.

Fabrication of electrode: Alumina slurry (0.05 μM) was used for polishing glassy carbon electrode (GCE). After polishing GCE was sonicated in ethanol for 10 min then rinsed with distilled water. About 0.176 g (0.045 M) CTAB was dispersed in 10 mL of 0.1 M H_2SO_4 and sonicated for 30 min to get a white suspension. The GCE was immersed in above prepared solution for depositing poly(CTAB) by cyclizing in the potential range -1 to 1.4 V for 10 cycles at scan rate 100 mV s^{-1} [18] (Fig. 1). The prepared electrode poly(CTAB)/GCE was washed and dried at room temperature.

RESULTS AND DISCUSSION

Characterization of modified electrode: The surface morphology of poly(CTAB) was examined by SEM as shown in Fig. 2a-b. The morphology of poly(CTAB) features a porous network structure with numerous nanoroads. The CTAB molecule dissolved in the solution aggregated in to rod like micelles over the surface of GCE. Thus, electropolymerization resulting in increased surface area, thereby enhancing its electrical conductivity. Fig. 2c shows EDS spectra of poly(CTAB) consists of peak corresponds to C, O, N, Br, which are in agreement with composition of poly(CTAB).

Fig. 3 shows FTIR spectra of poly(CTAB) film, bands at 2937 and 2833 cm^{-1} confirms the presence of CTAB chain. These two bands originate from the CH_3-CH_2 asymmetrical and symmetrical stretching vibrations, respectively. A sharp band at 1454 cm^{-1} corresponds to CH_3-CH_2 bending is also observed for poly(CTAB) [19].

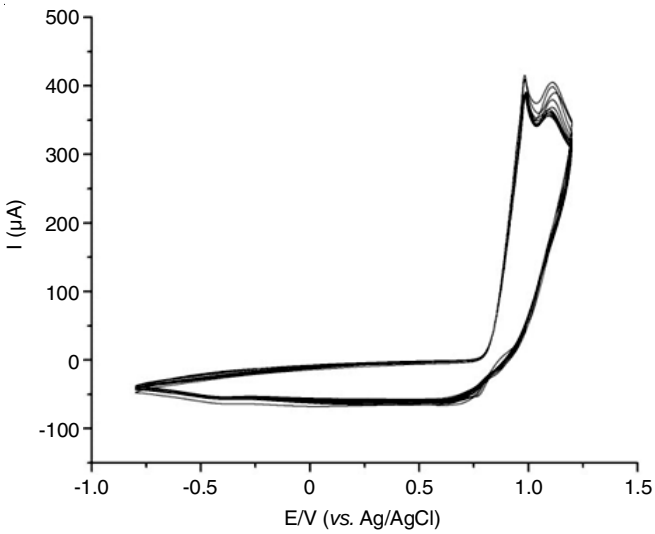

Fig. 1. Cyclic voltammogram of electro-polymerization of CTAB at scan rate 100 mV s^{-1} at a potential of -1 to 1.4 V for 10 cycles in 0.1 M H_2SO_4

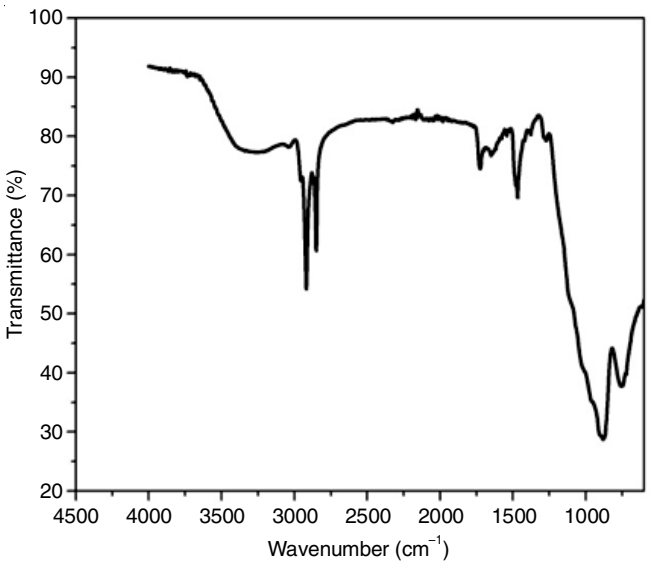

Fig. 3. FTIR spectra of poly(CTAB)

Electrochemical behaviour of morphine at poly(CTAB)/GCE: The electrochemical behaviour of morphine towards

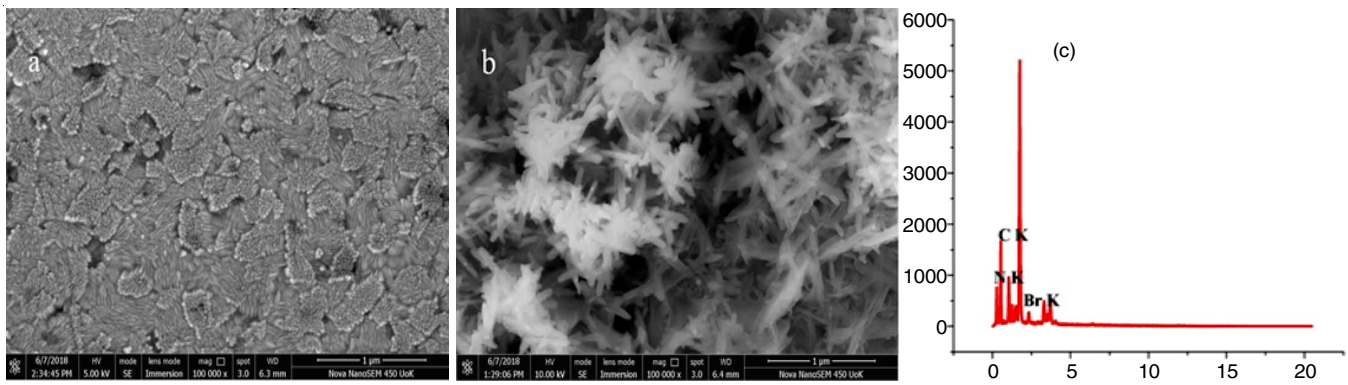

Fig. 2. FESEM images of (a) bare GCE (b) poly(CTAB) (c) energy dispersive X-ray (EDX) spectrum of poly(CTAB)

the fabricated electrode was investigated using cyclic voltammetry. The electrochemical response of morphine was examined in pH 7.0 PBS at bare GCE and poly(CTAB)/GCE using cyclic voltammetry in the potential range 0.2 to 1.2 V (*vs.* Ag/AgCl). As can be seen, two anodic peaks are observed at bare GCE (Fig. 4a) and at poly(CTAB)/GCE (Fig. 4b) of morphine. At bare GCE, morphine produced weak anodic peak at 0.617 V and 0.94 V corresponding to the oxidation of phenolic and tertiary amine group of morphine which indicates that electrotransfer rate at bare GCE is very slow. After modification with poly (CTAB), the anodic peak of morphine were lowered at 0.539V and at 0.88V. Moreover, the peak corresponding to phenolic group (0.539 V) at poly(CTAB) is very weak and not stable during subsequent scans. This may be attributed to the surfactant aided blocking behaviour of poly(CTAB) [20]. In addition, the peak current has considerably enhanced at poly (CTAB)/GCE compared to bare GCE. The lower oxidation potential and higher current response ensures the electrooxidation of morphine at a much faster rate which can be attributed to the enhanced surface area of electrode after modification with poly(CTAB). The phenolic group forms pseudomorphine and tertiary amine group gives normorphine as the major oxidative products [7,9]. The sensor poly(CTAB)/GCE shows high sensitvity and better catalytic activity towards the anodic oxidation of teriary amine group than phenolic group of morphine. There were no reduction peak in the reverse scan indicating the irreversible nature of electrode reaction.

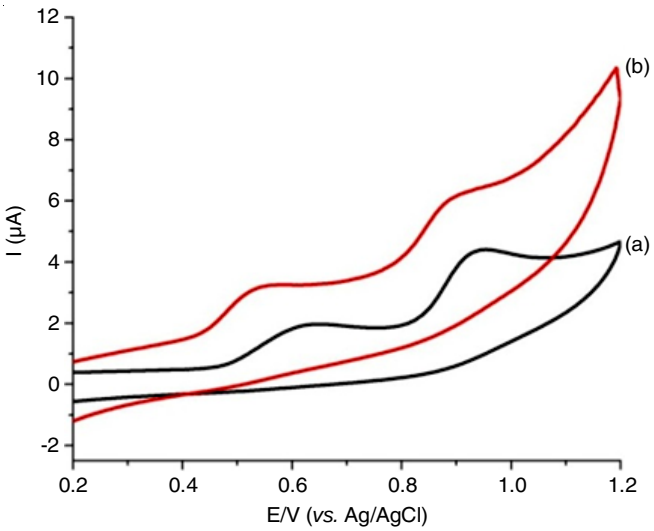

Fig. 4. Cyclic voltammetry of 0.1 mM morphine in 0.1 M (pH 7) PBS at (a) bare GCE (b) poly(CTAB)/GCE

Optimization of experimental condition

Effect of pH: The peak potential is very much depend on the pH of solution. The effect of pH on electrochemical performance of morphine was studied by using 0.1M PBS buffer solutions, ranging from pH 3.0-10, as the supporting electrolyte. The results showed that the values of peak potential shifted to more negative potentials with the increase of pH (Fig. 5). Such behaviour shows that protons took part in morphine oxidation. The slope value about - 49 mV/pH was obtained which is nearly equal to theoretical value of 59 mV indicating that equal number of protons and electrons involved in the oxidation of morphine at the modified electrode poly(CTAB)/GCE [21].

Effect of scan rate: The influence of scan rate (ν) on the peak current (I_{pa}) of morphine in pH 7.0 (0.1M PBS) at poly (CTAB)/GCE was examined in the range 10 to 300 mV s^{-1} as shown in Fig. 6a. The effect of scan rate was explained in terms of sensitive oxidation of tertiary amine group rather than phenolic group, which is suppressed and not stable during the subsequent scans [20,21] (Fig. 6a). The results showed a good linear relationship between the oxidation peak potential and logarithm of scan rate according to the equation, E_{pa} = 0.0682 log ν + 0.9251 (Fig. 6b). The Tafel plot was drawn using the following equation:

$$E_{pa} = 2.303RT/2(1-\alpha)\ nF \log \nu + \text{constant}$$

Based on the slope of 0.0682, the value of 'n' was obtained as 2 assuming electron transfer coefficient (α) to be 0.5. This indicates that the rate determining step of oxidation reaction of tertiary amine group of morphine in 0.1M (pH 7) PBS at poly (CTAB)/GCE involves two proton and two electron [1].

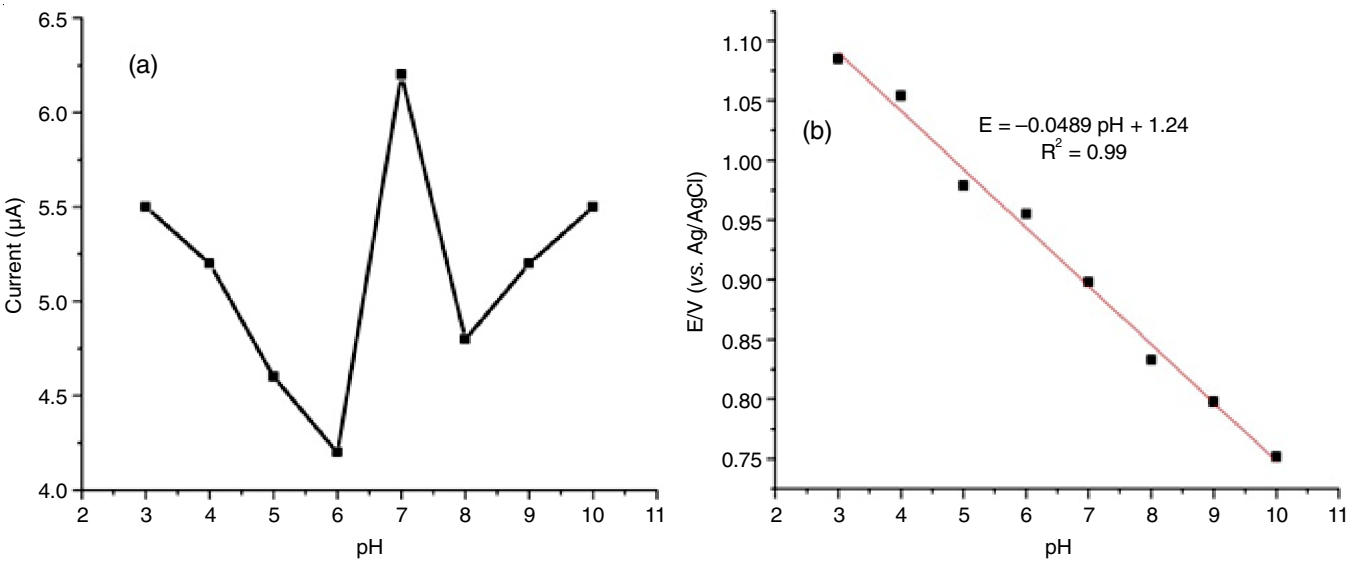

Fig. 5. (a) Cyclic voltammetry of 0.1 mM morphine at poly (CTAB)/GCE in PBS with different pH values (3-10) at scan rate 100 mV s^{-1} (b) Plot of pH *vs.* E_{pa}

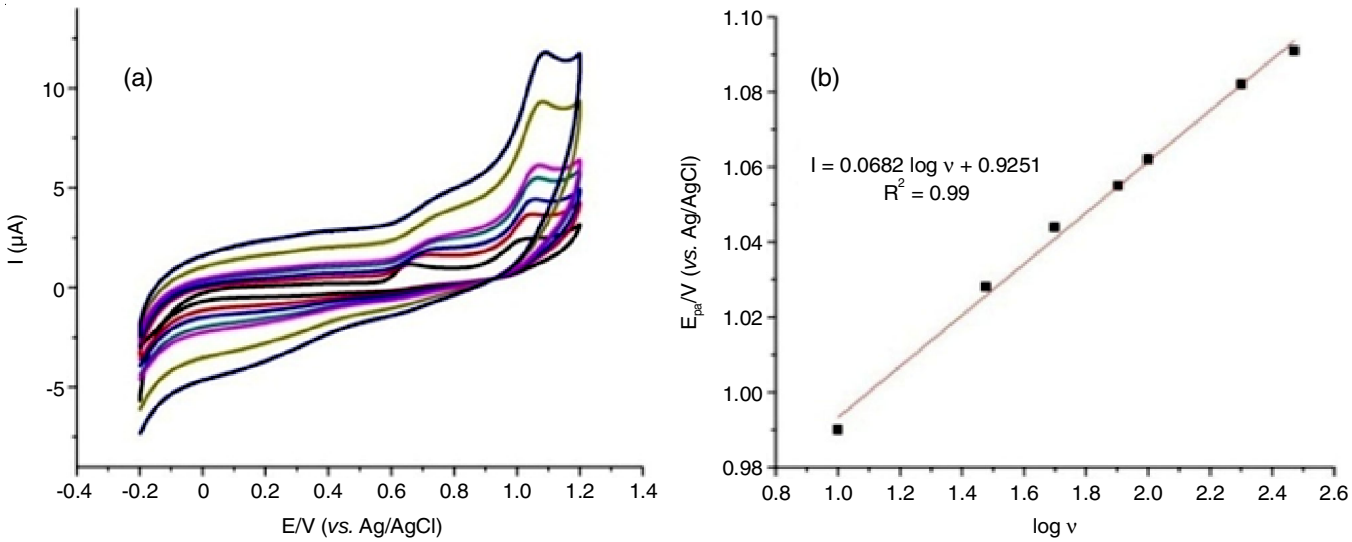

Fig. 6. (a) Cyclic voltammetry of 0.1 mM morphine in 0.1 M (pH 7) PBS at poly(CTAB)/GCE at different scan rates from 10 to 300 mV s^{-1} (b) Plot of log ν *vs.* E_p

Voltammetric analysis: Differential pulse voltammetry (DPV) was carried out for verifying the analytical performance of the fabricated electrode poly (CTAB) towards morphine. Fig. 7 shows the differential pulse voltammograms of different concentrations of morphine in 0.1 M PBS buffer solution of pH 7 under the optimum experimental conditions. The bio-sensor shows a linear relationship between anodic peak current and morphine concentration with a linear dynamic range 50 nM to 20 μmol L^{-1}. Regarding the resulted calibration curves and based on equation LOD=3S/b, the detection limit of 0.2 μ M was obtained for morphine [23]. The analytical performance of fabricated sensor was compared with previous reports as shown in Table-1.

Interference study: The modified electrode poly(CTAB)/GCE also examines the interference effect of morphine in presence of ascorbic acid and uric acid. Fig. 8 shows the oxidation of morphine (0.1 mM), ascorbic acid (1 mM) and uric acid (0.2 mM) on bare electrode and poly(CTAB) modified electrode in PBS pH 7 at scan rate 100 mV s^{-1} using cyclic voltammetry. The results demonstrated that at bare electrode, two anodic peaks at 0.464 V and 0.91 V are related to oxidation of mixture of ascorbic acid and uric acid and morphine. Whereas

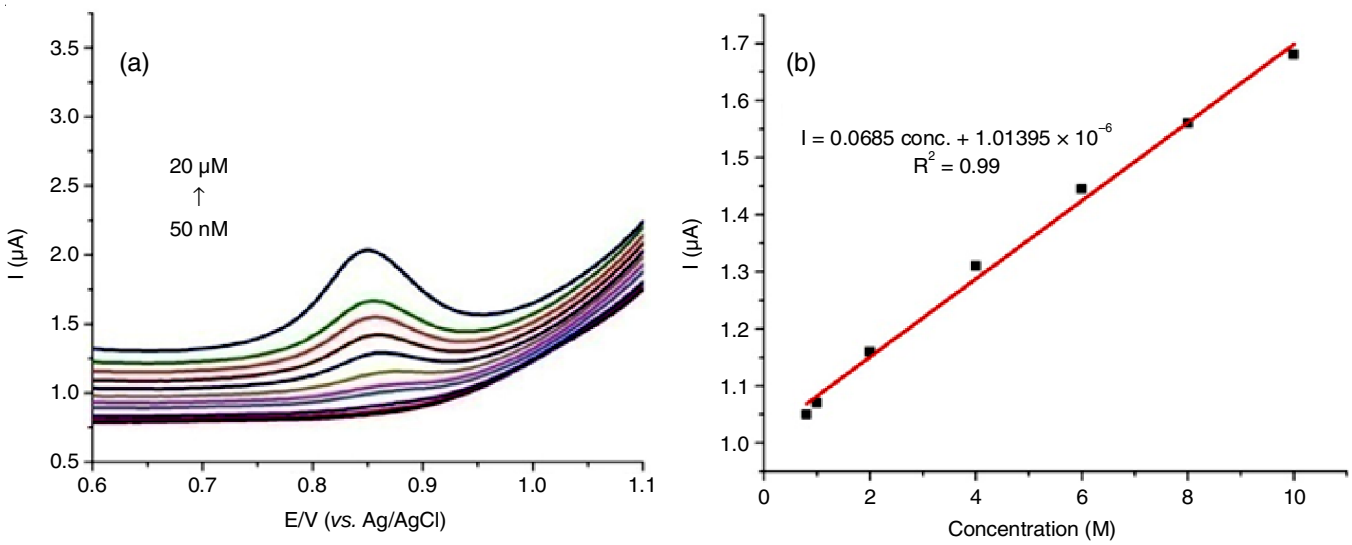

Fig. 7. (a) Differential pulse voltammograms of morphine at different concentrations 50 nM to 20 μM (b) Calibration graph of morphine

TABLE-1
COMPARISON OF THE ANALALYTICAL PERFORMANCE OF POLY(CTAB) MODIFIED ELECTRODE WITH OTHER REPORTS

Electrode used	Detection limit (μM)	References
MWCNTs/Chitosan modified glassy carbon electrode	0.24	[12]
Graphene nanosheet glassy carbon electrode	0.40	[13]
Exfoliated graphene oxide/screen printed electrode	2.50	[25]
Hydrogel/ carbon paste electrode	1.00	[26]
Poly(CTAB) modified glassy carbon electrode	0.20	Present Work

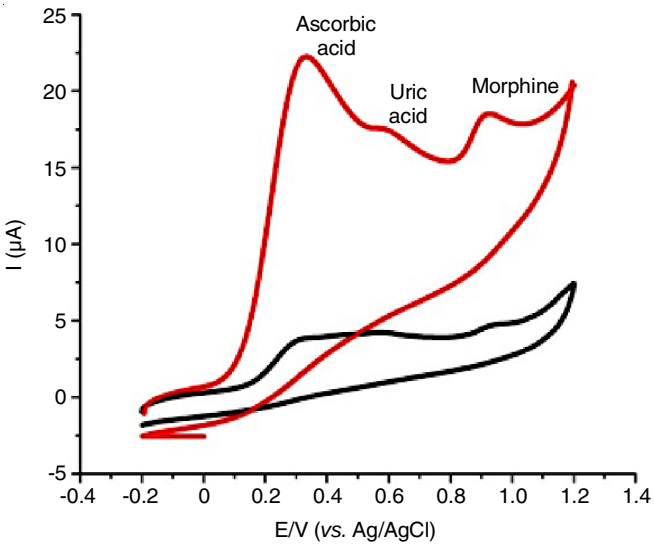

Fig. 8. Cyclic voltammetry of bare and poly (CTAB)/GCE for a mixture of morphine (0.1 mM), ascorbic acid (1 mM) and uric acid (0.2 mM) PBS buffer pH 7 at a scan rate 100 mV s^{-1}

at poly (CTAB)/GCE modified electrode three well resolved peaks at potentials 0.90 V for morphine, 0.343 V for ascorbic acid and 0.59 V for uric acid are obtained. From these results, the selectivity of the method was verified [24].

Conclusion

The present study focus on the fabrication of sensor with poly(CTAB) by one step electropolymerization for the effective determination of morphine. The electrochemical performance of modified sensor illustrates the electrooxidation of morphine through its *tertiary*-amino group rather than phenolic group. The sensor poly(CTAB)/GCE exhibited a remarkable effect on the voltammetric response of morphine due to its excellent electrocatalytic activity. A detection limit of 0.2 µM with wide linear range of concentrations 50 nM to 20 µM was observed. The results confirmed that poly(CTAB) modified electrode provide an excellent platform for the electrochemical detection of similar molecules.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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